

TECHNICAL PROGRESS REPORT, UNIVERSITY COAL RESEARCH PROGRAM

TITLE: **CONTRIBUTION OF SEMI-VOLATILE ORGANIC MATERIAL
TO AMBIENT PM_{2.5}**

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1. EXECUTIVE SUMMARY

The research program funded by the University Coal Research Program at Brigham Young University determined the composition of fine particulate material in the atmosphere with emphasis on the contribution of semi-volatile organic material to ambient $PM_{2.5}$ at the NETL Pittsburgh Fine Particulate Characterization sampling site. This material may be important to human health and is not determined by conventional single filter samplers. A sampler combining particle concentrator and diffusion denuder technology, the PC-BOSS, was used in the study. During the first year of the program the PC-BOSS was installed at the NETL site and the first of an intended two year sampling program was conducted. Samples were collected every day with the PC-BOSS from November 1999 through December 2000. Focus in the second year of sampling was on the determination of the diurnal pattern of pollution, so samples were collected multiple times each day for selected intensive studies each season from January 2001 through February 2002. Focus in the last portion of the program has been on completion of the data analysis and preparation of manuscripts related to the results of the two-year sampling study. A total of thirteen manuscripts have now been published or submitted for publication related to the research. The results obtained in the research program indicate that both the semi-volatile and nonvolatile organic material in the fine particles sampled at the NETL site originate from mobile emissions in the local area. The majority of the semi-volatile organic material in fine particles is secondary in nature, being formed from photochemical processes in the atmosphere. In contrast, the fine particulate sulfate does not originate from the local area but is transported into the study region, mostly from sources in the Ohio River Valley. There was sufficient information contained in the results obtained for sophisticated source apportionment analyses to be done with the data. That effort has been completed and apportionment analysis and related manuscripts submitted for publication.

2. ABSTRACT

Both annual 24-h average and seasonal diurnal samples collected at NETL during the research program have been analyzed. The fine particulate components determined include $PM_{2.5}$ mass, ammonium sulfate, ammonium nitrate, elemental and organic carbonaceous material and trace elements. The analysis of the nitrate and organic material includes both the identification of nonvolatile material retained by the particle collection filter and semi-volatile material lost from the particles during sample collection. The results obtained in these analyses indicate that both the semi-volatile and nonvolatile organic material in the fine particles sampled at the NETL site originate from mobile emissions in the local area. However, the majority of the nonvolatile material is associated with primary emissions and the majority of the semi-volatile material is secondary, being formed from photochemical processes in the atmosphere. In contrast, the fine particulate sulfate does not originate from the local area but is transported into the study region, mostly from sources in the Ohio River Valley. These observations have been supported by both detailed meteorological and apportionment analysis of the data.

3. OBJECTIVE

The hypothesis of the research program was that fine particulate mass will be significantly under-determined in urban environments using single filter samplers such as the PM_{2.5} Federal Reference Method (FRM) because of the loss of semi-volatile organic compounds (SVOC) from the particles during sampling and storage. It was postulated that fine particulate mass, including the semi-volatile fine particulate organic species, are an appropriate surrogate for the components of fine particles which are associated with observed mortality and morbidity effects in epidemiological studies. Further, it is postulated that the most important fraction of the semi-volatile organic material with respect to exacerbation of health problems will be semi-volatile secondary compounds formed from reactions of volatile organic material with ozone and nitrogen oxides. Under-determination of these semi-volatile species will tend to over emphasize the importance of non-volatile fine particulate components such as sulfate or may reduce the significance of correlations with measured health effects. The proposed research program was a cooperative effort between BYU and NETL, Pittsburgh to determine the contribution of semi-volatile particulate organic compounds (SVOC) to total ambient suspended fine particulate mass.

The following tasks have been completed.

1. Data have been obtained for two sampling programs at the NETL facility in Pittsburgh. The first sampling program was a year-long effort from November 1999 through December 2000 to identify the daily contribution of semi-volatile organic material to ambient PM_{2.5} and determine the meteorological conditions which are associated with formation of high concentrations of fine particulate SVOC
2. The second year-long program involved the determination of diurnal variations in total fine particulate SVOC and the contribution of nitrogen oxide containing SVOC to PM_{2.5} under meteorological conditions which lead to high fine particulate SVOC.
3. Samples collected in 1. and 2. have been analyzed and the results used in the preparation of the manuscripts listed in Section 6. of this report.

4. ACCOMPLISHMENTS

Sample collection during the first year at NETL has been completed. Samples collected beginning in late November 1999 and continuing through December 2000. During the first year's sampling program, 24-hour PM_{2.5} mass and chemical composition were determined with a PC-BOSS particle concentrator diffusion denuder sampler for the determination and characterization of fine particulate mass, including semi-volatile organic material lost from fine particles during sampling with a filter. The composition of the collected fine particles (sulfate, nitrate, acidity, ammonium ion, semi-volatile and non-volatile organic material, and soot) have been determined for these samples. The results for this effort have been published or submitted for publication. The results obtained during this period have been compared to results obtained using the EPA FRM PM_{2.5}

sampler and the R&P TEOM monitor. The comparison shows that significant fine particulate semi-volatile organic material is not determined using these two samplers. During the second year sampling effort, the diurnal pattern of $PM_{2.5}$ mass and composition were studied during both summer and winter intensive sampling periods. During these studies, samples were obtained at both the NETL sampling site and at the EPA Supersite operated by Carnegie Mellon University near the CMU campus. The results from the comparison of the data at the two sites indicates the following:

1. Sulfate is dominantly a secondary pollutant, transported to the NETL site from distant sources, primarily in the Ohio River Valley.
2. Both primary and secondary and sources from automobiles and diesel engines contribute to the fine particulate organic material seen at the two sites.
3. The atmospheric chemistry at the NETL site is dominated by the formation of semi-volatile secondary organic material.
4. The atmospheric chemistry at the CMU site is dominated by NO_x chemistry.

We have completed all planned manuscript related to the study.

6. SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

The combined experiments conducted with UCR support have quantified the semi-volatile organic species lost from particles using conventional single filter samplers, identify the conditions under which substantial amounts of SVOC are present in $PM_{2.5}$ and determine conditions which lead to the presence of substantial amounts of potentially toxic NO_x -SVOC material in ambient fine particles. Identification of the extent of, composition of, and conditions under which particulate semi-volatile organic species are lost during sampling should allow a better assessment of the role which these major fine particulate species may play in the etiology of mortality and morbidity effects associated with exposure to fine particles. This will allow for the development of appropriate attainment strategies, the collection of better exposure data and an improvement in risk assessment analyses.

7. MANUSCRIPTS

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